

RAPID, EASY MULTIELEMENT ANALYSIS OF WHOLE COAL VIA SLURRY-INJECTION ATOMIC ABSORPTION SPECTROPHOTOMETRY

James E. O'Reilly and Donald G. Hicks

Department of Chemistry, University of Kentucky, Lexington,
Ky., 40506; and The Institute for Mining & Minerals Research,
Kentucky Center for Energy Research Laboratory, P.O. Box 13015,
Lexington, Ky., 40583.

INTRODUCTION

In recent years, a few laboratories have reported on the use of flame atomic absorption/emission methods for the analysis of solids directly, bypassing normal ashing and dissolution steps(1-5). However, not all these workers made attempts to achieve quantitative results. For example, although the early paper by Harrison(4) and the recent one by Willis(5) are quite significant, neither reported any quantitative analyses of standard or non-standard analyzed samples! Furthermore, no efforts have been made thus far to determine functional limits of detection and analysis for a wide variety of elements in any one particularly significant solid matrix such as coal. Atomic absorption(AA) procedures involving non-flame furnace atomization techniques seem to have been more widely investigated(6-13).

The need to analyze coal for major, minor, and trace-level elements has been underscored by the Clean Air Act of 1970(14) and the Toxic Substances Control Act of 1976(15,16). Concentrations of trace elements are of great interest in the geological characterization of coals(17), and Hook(18) has emphasized the significance of metals content of coal in determining the quality of industrial products such as coke, iron, and steel. Moreover, the U.S. National Bureau of Standards has recently introduced bituminous and sub-bituminous coal Standard Reference Materials (19,20) having certified concentration values for 14 trace metals. A survey has shown that 70 % of the millions of geochemical exploration samples collected annually have been analyzed by AA procedures(21). But conventional AA analysis procedures are plagued by lengthy sample preparation steps, usually involving a high or low-temperature ashing for many hours, followed by a prolonged dissolution in mixed acids. Even for a "rush" analysis, the turnaround time is nearly 2 days from receipt of samples.

Therefore, we have developed an atomic absorption method for the direct analysis of whole coal by injection of powdered coal slurries into either flames or graphite furnaces. This paper greatly expands the preliminary observations of O'Reilly(22) on the slurry-injection approach to flame AA analysis of coal. Our work is oriented toward a comprehensive exploration of the capabilities of this general approach for determining a wide variety of elements in some difficult-to-digest solid matrices such as coal, coal ash, oil shale, limestone, pigments, glasses, and selected ores. That is, solid matrices with "relatively" constant major component compositions.

EXPERIMENTAL

Apparatus and Reagents: All absorption and emission signals were measured using a non-modified Varian Model AA-6 atomic absorption spectrophotometer equipped with a Model BC-6 H₂-lamp background corrector, Model CRA-90 graphite tube/cup atomizer system, and a high quality strip chart recorder capable of expanding the 100 mv output absorbance signal by 100x in several steps. A standard Varian premix

burner with single-slot "high solids" heads was used throughout for flame atomization studies. As supplied, nebulizer intake capillaries had quite variable I.D. values. To minimize clogging, only those with I.D. greater than 35 μ m were utilized. To decrease the frequency of removing solid particles constantly collecting therein, a large conical suction flask was filled with water and used as a burner "drain trap" at floor level. A length of 8 mm glass tubing was inserted through a one-hole rubber stopper to a point about 5 inches below the water surface, and also connected to the burner chamber. A plastic tube ran from the flask side arm to a drain in the floor. The critical, final comminution of analytical samples was accomplished by use of a swing-mill (Spex Model 8510 Shatterbox) with 3.7 x 2.5 inch hardened steel or tungsten carbide(WC) grinding containers.

Certified atomic absorption standard solutions (Fisher Scientific) were used to prepare aqueous standards. A 10 % by weight stock solution of Triton X-100(Rohm & Haas scintillation grade) wetting agent was prepared and diluted daily as needed to 0.2 % or 0.5 % with distilled and doubly deionized water. Other materials were reagent grade.

Reference standard coals of nominal sub-60 mesh(-250 μ m) particle size were prepared from several eastern Kentucky bituminous coal samples. Ten to twenty pounds of each of these raw coals was put through (a) a standard jaw crusher, (b) a roller-mill, and (c) a Holmes Model 500 rotor-beater type of pulverizer equipped with a screen allowing output particles of 60-mesh or smaller. After tumbling each total sample 2 hrs, they were dried briefly at 110°C to remove surface moisture. The reference standard coals were then analyzed for content of several elements by conventional AA procedures involving 24-hr low-temperature oxygen-plasma ashing(23,24) and dissolution of the ash after treatment with aqua regia/HF in a teflon bomb(25,26) or fusion with lithium tetraborate (27,28). Analysis of NBS-SRM coal as an unknown and studies on the linearity of AA signals versus concentration made use of these samples.

Analysis Procedure: The grinding chamber of the Spex swing-mill was "dry-cleaned" initially, and also between samples, by a 2-min milling of about 6 mL of the new coal sample to be analyzed. After discarding the resulting powder, the chamber was quickly wiped with laboratory tissue and blown out with a jet of dry air. Roughly 10 mL of the new coal sample was then added to the container and pulverized for 10 minutes. The majority of the powdered sample was dumped into a 325-mesh(44 μ m) metal screen sieve with a 3-inch brass body, then shaken and bumped by hand for 1.5 minutes. Two-thirds or more of the solid typically passed the screen. The -44 μ m powder which collected in the bottom pan was covered with a snug-fitting lid, shaken vigorously for about 10 sec, and tumbled 10-12 times. Analytical samples in the range of 0.1 to 2.5 g were placed in 150-mL beakers. Using graduated cylinders or repipets, 30 to 100 mL of 0.5 % Triton X-100 slurring solution was gently added to produce slurries containing 0.1 to 8.0 grams coal per 100 mL slurring liquid(0.1 % to 8 % wt/vol solids). Actually, with the burner slot parallel to the light beam, most elements in most coal samples could be determined using slurries of 0.3 %, 5 %, or 8 % solids. Slurries of reference standard coals and unknowns were always prepared to contain approximately the same % solids. Samples were then stirred magnetically for about 30 minutes prior to aspiration into the burner. Absorbance measurements, made while stirring the slurries gently, were corrected for non-atomic "background" absorption using broad-band emission from an H₂-arc lamp. Absorbances of standard and unknown

coal slurries were normalized to the same % solids value which was chosen to be near the solids level of the slurries actually prepared. Element concentrations in the unknowns were determined from best-fit calibration curves constructed from standards, or from simple ratios of absorbances of standards and unknowns with subsequent averaging.

When analyzing coal by non-flame graphite furnace atomization techniques, suspensions containing 0.2 to 8.0 g of unsieved powdered coal per 100 mL total slurry volume were prepared by dilution in volumetric containers. After brief mixing, slurries were transferred to wide mouth containers and stirred a few minutes. Adding 5 to 25 μ L of the slurries to the graphite tube or cup provides a functionally accurate and rapid method to measure 10 to 2000 μ g of powdered coal sample.

RESULTS AND DISCUSSION

Sample Comminution Studies: Of several types of grinding devices examined, a swing-mill (Spex "Shatterbox") was found to be generally superior after considering such factors as (a) production of a very high percentage of really fine (-325 mesh) particles, (b) grinding 7 to 45 grams of sample, (c) short milling time, (d) number of samples milled simultaneously, and (e) general ease of operation and reproducibility. Table I illustrates that absorbances of samples ball-milled 60 min are significantly lower than those for samples pulverized 12 min in any swing-mill container. Usually, slurries made from unsieved coal ground in the swing-mill WC chamber did not clog burner capillaries. But clogging did occur often enough for us to recommend a brief partial sieving in the analytical procedure. The optimum time (Fig. 1) to grind 12 mL of coal having a 44-250 μ m starting range of particle sizes was found to be 12-15 minutes, although grinding times as short as 5 min will produce suitable samples when sieved. Since absorption has been shown to increase with decreasing particle size(5), 12 min in a swing-mill WC dish apparently results in a maximum state of subdivision of particles. Prior to this maximum absorbance grinding time, the -325 mesh powder exhibits a signal slightly greater than that of the unsieved samples. But after 12 minutes, the two types of samples show no difference in signal. To minimize clogging, 30-min of intermittent stirring is recommended after first mixing the slurry, particularly for water-based slurries of higher solids content. However, analytically useful slurries are obtainable after only 5-10 min stirring of either water-based suspensions with lower % solids or organic solvent mixtures of any solids level. Slurries having 8 % solids in a water base or 20 % solids in organic solvents have been aspirated a few minutes without clogging a 0.4 mm I.D. burner capillary. Regardless of the % solids, the rate of slurry aspiration is essentially the same as the uptake rate of the particular slurrying liquid (within 1 % to 2 %). Although clogging factors are discussed here, it is emphasized that it rarely happened when following routine analysis procedures.

Analysis By Flame Atomization: Best-fit calibration curves, obtained at some particular % solids level, are generally linear over a reasonable concentration range---as illustrated by Figures 2 and 3. Individual points resulting from different standard coals show a small, but highly reproducible, scatter about the line. We interpret this to be caused by relatively small matrix variation effects. For elements tested, slurry calibration curves have the same general shape. That is, they exhibit the same relative positioning of data points whether obtained (a) in $N_2O-C_2H_2$ or air- C_2H_2 flames, (b) from unsieved or partially sieved powders, (c) after 15 min milling in a swing-mill or 2 hr in a

rolling-jar ball-mill, or (d) after 20 min or 3 hrs stirring. Strong emission signals for several elements were obtained from coal slurries. In the case of sodium, the AA calibration curve had the same shape as one obtained from atomic emission measurements. Precisions attainable by this slurry-injection AA approach are quite good as seen in Table II, and are similar to those observed for replicate determinations on purely aqueous standards. Relative standard deviations (RSD) are typically 1 % of the mean for elements with strong signals, and 3-4 % when scale expansion is required.

For some elements whose coal slurry AA signals are quite small, considerable scale expansion is necessary and non-atomic "background" absorbance becomes significant (Fig. 3). Experimental observations shown in Table III suggest that this apparent absorption is primarily caused by light scattering from the solid particles. This "background" signal increases linearly with increasing solids level, is relatively constant from one coal to another, is greater when measured near the top of the burner, is much greater when the slurry is aspirated by non-burning gases (Table III), decreases gradually as wavelength changes from 200 nm to 600 nm (Table III), has the same magnitude whether measured with line or broadband light sources (Table III), increases with increasing slurry aspiration rate, is greater for coal sieved through a screen with larger openings (i.e. larger particles), is much less in the $N_2O-C_2H_2$ flame than in the air- C_2H_2 flame, and has a maximum observed absorbance of 0.002/1 % solids---this latter data in accord with Willis⁵ value for pulverized rocks.

Figure 4 indicates that conventional atomic absorption sensitivities (ppm at which $Abs. = 0.0044$) for elements in the NBS-1632 coal matrix increase in the same general order as AA sensitivities determined in aqueous solution. Atomization efficiencies relative to water media were determined as $\% \text{ atomization} = (100)(\text{slurry absorbance})/(\text{aqueous solution absorbance})$ at equal effective concentrations of the test element. These efficiencies for coal ranged between 16 % and 24 % of those obtainable from aqueous solution. Apparently, the NBS-1632 coal matrix (and perhaps others) does not drastically affect the signal of one element relative to another.

Flame response profile studies have shown that elements generally exhibit a maximum absorbance at a point higher in a flame when slurries are fed in than when aqueous solutions are aspirated (Fig. 5). As can be seen in Figure 6, the relative atomization efficiency in a flame also increases with increasing height above the burner. The % atomization of slurries increases more rapidly with increasing height in the $N_2O-C_2H_2$ vs air- C_2H_2 flame, and, the height of maximum absorbance is nearer the top of the burner in the $N_2O-C_2H_2$ vs air- C_2H_2 flame; both observations being in contrast with the greater aspiration rate of the $N_2O-C_2H_2$ burner. Along with the fact of lower non-atomic background absorbance therein, these data indicate that the $N_2O-C_2H_2$ flame is more efficient than the air- C_2H_2 flame in decomposing solid particles.

Of 33 elements studied, 23 were found to have sufficient sensitivity to be determined by flame atomization at levels normally encountered in coal (Al, Si, Fe, K, Ca, Mg, Na, Ti---Ba, Be, Cu, Cr, Co, Eu, Li, Mn, Ni, Pb, Rb, Sr, V, Yb, and Zn). Eu and Yb were detected by their emission signals from $N_2O-C_2H_2$ flames. Ag, As, Bi, Cd, Mo, P, Pd, Se, Sn, and Te were not detected with sufficient sensitivity. Utilizing

flame atomization, concentrations of 16 elements have been determined in NBS-1632 SRM coal with moderate accuracies of ± 5 to 25% error (Table IV). Although NBS-1632 is a relatively uniform blend of several coals, it is to be noted that the eastern Kentucky coals used as standards were not uniform. When considering sample-to-sample variations, it has been observed that slurry absorbances of Si and Al increase as ash content of the coal increases. But, correlations are not linear. Some other elements tested (Fe, Ti, Mg, Ca, K, Na, Ba, Sr) do not consistently show a similar correlation. Analysis of high speed photographs of flames has shown that the rise velocity of the larger of the $-44 \mu\text{m}$ coal particles near the top of the burner is essentially the same as the streaming velocity of the gases through the burner slot.

SUMMARY AND CONCLUSIONS

Most of our work has concerned flame atomization AA procedures, which are generally faster and more convenient than non-flame electrothermal atomization techniques. A recent brief report by Gladney(10) showed that Be in coal could be accurately determined by graphite furnace techniques, with observed precisions around 7.5 % RSD. Our work confirms determination of this particular element, and also shows that injection of μL amounts of slurries into a graphite cup/tube is a rapid and very reproducible way to circumvent microbalance weighings! In general, it appears that powdered coal slurries may be analyzed (in these devices) for elements which allow higher ashing and atomization cycle temperatures. Using a 2.5 mm I.D. graphite cup for atomization, 8 replicate determinations on 10- μL aliquots from a 1 % solids slurry ($-44 \mu\text{m}$ coal) resulted in a relative standard deviation of 3.2%.

Ease of sample preparation plus greatly increased speed of analysis using a commonly available instrument are the main advantages of this slurry injection AA method for coal analysis. As an example, the turnaround time for determining the concentrations of 4 elements in 6 samples can be reduced to 2 hrs from the current 2 days required by conventional AA procedures! Some operator time is also saved. The technique is useful for extremely fast single element scanning, which would allow more frequent and widespread sampling of coal shipped in large vessels. Although multielement scanning is a sequential process, it is rapid and does compete in total analysis time with X-ray fluorescence techniques, for instance. Assuming 10-12 min XRF instrument time per sample count period, and high and low energy counting on each sample, the XRF and slurry-injection AA methods both need about $\frac{1}{2}$ day to determine 12 elements in 6 samples. The price paid for this speed is the achievement of only modest accuracy. However, slurry-injection AA accuracies might be improved over those implied by the data in Table IV if standards and unknowns are matched somewhat better with respect to approximate ash content or general type of coal. Accuracies are certainly good enough for geochemical explorations, and are actually in the range of values reported(17) for conventional AA determinations.

ACKNOWLEDGEMENTS

We are grateful to Henry E. Francis, Karen Moore, and Sayra Russell for selected analyses, and to Dennis Sparks for initial preparation of some coal samples. Financial support for this project was provided by the Kentucky Center for Energy Research and the Institute for Mining and Minerals Research, and by Georgia State University (sabbatical leave for DGH).

REFERENCES

1. P. T. Gilbert, Anal. Chem., **34**, 1025 (1962).
2. J. L. Mason, Anal. Chem., **35**, 874 (1963).
3. V. I. Lebedev, Zh. Anal. Khim., **24**, 337 (1969).
4. W. W. Harrison and P. O. Juliano, Anal. Chem., **43**, 248 (1971).
5. J. B. Willis, Anal. Chem., **47**, 1752 (1975).
6. F. J. Langmyhr, J. R. Stubergh, Y. Thomassen, J. E. Hanssen, and J. Dolezal, Anal. Chim. Acta, **71**, 35 (1974).
7. F. J. Langmyhr, R. Solberg, and L. T. Wold, Anal. Chim. Acta, **69**, 267 (1974).
8. E. L. Henn, Anal. Chim. Acta, **73**, 273 (1974).
9. D. A. Lord, J. W. McLaren, and R. C. Wheeler, Anal. Chem., **49**, 257 (1977).
10. E. S. Gladney, At. Absorpt. Newsl., **16**, 42 (1977).
11. D. D. Siemer and H. Wei, Anal. Chem., **50**, 147 (1978).
12. B. V. L'vov, Talanta, **23**, 109 (1976).
13. F. J. Langmyhr, Talanta, **24**, 277 (1977).
14. U. S. Clean Air Act of 1970, Public Law 91-604, Dec 31, 1970.
15. U. S. Toxic Substances Control Act of 1976, Public Law 94-469, Sec. 4, 10, 27.
16. R. M. Druley and G. L. Ordway, Eds., "The Toxic Substances Control Act," Bureau of National Affairs, Washington, D.C., 1977.
17. H. J. Gluskoter, R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn, "Trace Elements in Coal: Occurrence and Distribution," Illinois State Geological Survey Circular 499, 154 pp., 1977.
18. W. Hook, Pure Appl. Chem., **49**, 1465 (1976).
19. NBS-1632a and NBS-1635 SRM Data sheets, National Bureau of Standards, U. S. Department of Commerce, Washington, D.C., 1978.
20. J. M. Ondov, W. H. Zoller, L. Olmez, N. K. Aras, G. E. Gordon, L. A. Rancitelli, K. H. Abel, R. H. Filby, K. R. Shah, and R. C. Ragaini, Anal. Chem., **47**, 1102 (1975).
21. J. S. Webb and M. Thompson, Pure Appl. Chem., **49**, 1507 (1976).
22. J. E. O'Reilly and M. A. Hale, Anal. Lett., **10**, 1095 (1977).
23. H. J. Gluskoter, Fuel, **44**, 285 (1965).
24. C. E. Gleit and W. D. Holland, Anal. Chem., **34**, 1454 (1962).
25. B. Bernas, Anal. Chem., **40**, 1683 (1968).
26. B. Bernas, Amer. Lab., **5** (8), 41 (1973).
27. R. B. Muter and L. L. Nice, in "Trace Elements in Fuel," S. P. Babu, Ed., American Chemical Society, Washington, D.C., 1975.
28. J. H. Medlin, N. H. Suhr, and J. B. Bodkin, At. Absorpt. Newsl., **8**, 25 (1969).

FIGURE CAPTIONS

- Figure 1. Effect of grinding time in a Spex Shatterbox (tungsten-carbide container) on the atomic absorbance of several elements in one coal sample that was originally 60/325 mesh (44-250 μ m particle diameters). The solid circles are for unsieved final samples, the open circles for a final sample partially screened through a 325-mesh sieve. Conditions: nitrous oxide-acetylene flame; 1% wt/vol coal slurry; wavelengths = 285.2, 248.3, and 213.9 nm for Mg, Fe, and Zn.
- Figure 2. Calibration curve for analysis of zinc in whole coal. Conditions: air-acetylene flame, 0.4% wt/vol coal slurry in 0.2% Triton X-100, coal ground in a tungsten-carbide swing-mill.
- Figure 3. Calibration curve for analysis of manganese in whole coal illustrating correction for background absorbance. A: Absorbance of coal slurries without correction for background absorbance. B: Flame background absorption (particulate scattering) of aspirated coal slurries at 380 nm measured separately with a hydrogen-arc lamp mounted in place of a hollow-cathode lamp. C: The resultant background-corrected calibration curve. Conditions: air-acetylene flame, 3% wt/vol coal slurry in 0.2% Triton X-100, coal samples ball-milled, -325-mesh fraction.

Figure 4. Atomic absorption sensitivities ($A = 0.0044$) for a number of elements in NBS-1632 coal slurry versus the experimental sensitivity for those elements in purely aqueous standard solutions. The two lines represent effective atomization efficiencies of an element in a coal slurry of 16 and 24% that in aqueous solution. Conditions: nitrous oxide-acetylene flame except for Rb; coal slurries were of different solids levels in 0.2% Triton X-100; coal ground in a tungsten-carbide swing-mill.

Figure 5. Effect of measurement height in the flame on the atomic absorbance of iron in aqueous solution and in a coal matrix. Circles--in an air/acetylene flame; triangles--in a nitrous oxide-acetylene flame. Solid points--0.50% coal slurry in 0.5% Triton X-100; open points--aqueous 5 ppm iron solution. Conditions: The coal (1.07% Fe content) was ground 15 min in a steel swing-mill and sieved through a 200-mesh (75 μ m) screen.

Figure 6. Effect of measurement height in the flame on the relative atomization efficiency ($\epsilon_{rel} \times 100$) of iron in a coal matrix. Conditions same as in Figure 5.

Table I. Atomic Absorbance of Certain Elements vs. Grinding-Preparation Method^a

Grinding- Preparation Method	Grinding Time, min	Sieving ^b	Element ^c				
			Mg(NA)	Al(NA)	Si(NA)	Fe(NA)	Fe(AA)
Ball mill	60	yes	0.661	0.299	0.212	0.148	0.290
Swing-mill (steel)	12	yes	0.831	0.533	0.301	0.188	0.468
Swing-mill (WC)	12	yes	0.860	0.575	0.314	0.198	0.504
Swing-mill (WC)	12	no	0.862	0.577	0.317	0.195	0.504

^aThe same sample of coal was used in all grinding tests. ^bAfter grinding, the subsample was partially sieved through a 325-mesh screen (<44 μ m diameter particles). Conditions: 2% wt/vol coal slurries in 0.2% Triton X-100. ^cAbsorbances are the average of at least three measurements; AA = air-acetylene, NA = nitrous oxide-acetylene flame. The normal atomic absorption wavelengths were used for the four elements studied. WC = tungsten carbide grinding chamber.

Table II. Precision of Atomic-Absorption Signal Intensities^a

Element	Series A	Series B	Series C
	RSD ^b	RSD	RSD
Fe	1.1	0.90	0.95
Zn	2.5	2.7	2.3
Mg	0.72	-	0.76
K	-	-	0.93

^aIn the A series of replicate analyses, nine 15-mL subsamples of a particular -60 mesh coal were milled 15 min in the swing-mill hardened-steel container and sieved 1.5 min by hand through a 200-mesh (75 μ m) screen. Series B was 10 subsamples of the same coal pulverized 2 hr in a rolling-jar ball-mill, and then sieved 2 min by hand through a 400-mesh (38 μ m) screen. Series C consisted of nine 12-mL subsamples of a different coal milled 10 min in the Shatterbox WC container, and then sieved 1.5 min by hand through a 325-mesh (44 μ m) screen. Series A and C employed an air-C₂H₂ flame while series B used the N₂O-C₂H₂ flame.

^bRSD = relative standard deviation as percent of the average.

Table III. Background Absorbance of a Coal Slurry at Several Wavelengths^a

Wavelength, nm	Lamp ^b	Absorbance, $\times 10^3$		
		N ₂ O-C ₂ H ₂ Flame	Air-C ₂ H ₂ Flame	Air-C ₂ H ₂ No Flame ^c
207.5	HC	1.5	4.7	12.4
214	H ₂	---	4.8	---
231.7	HC	1.3	4.9	12.9
267.3	HC	1.1	3.3	11.9
280	H ₂	---	3.2	---
326.1	HC	---	2.9	---
358	H ₂	---	2.2	---
391.0	HC	0.6	2.6	9.5
450	H ₂	---	1.8	---
459.3	HC	---	2.0	---
610.4	HC	---	1.6	---

^a5% wt/vol slurry in 0.5% Triton X-100. Coal was ground 15 min in a steel swing-mill, and sieved through a 200-mesh sieve. Dash means measurement not made.

^bHC = isolated line from a hollow-cathode lamp; H₂ = Hydrogen arc lamp. ^cFlame not lit, but gases flowing on the air-C₂H₂ burner head; zero absorbance set with 0.5% Triton X-100 aspirating.

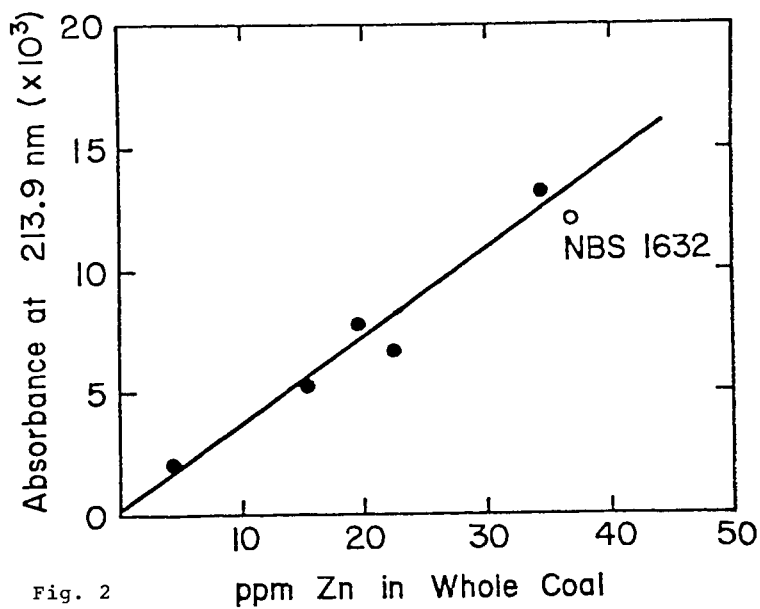
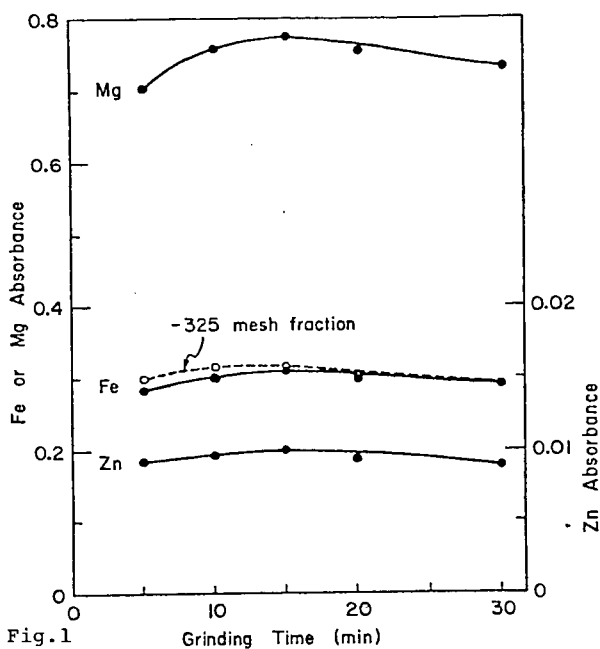
Table IV. Analysis of NBS-1632 Bituminous Coal SRM by Slurry-Injection
Atomic Absorption Spectrophotometry^a

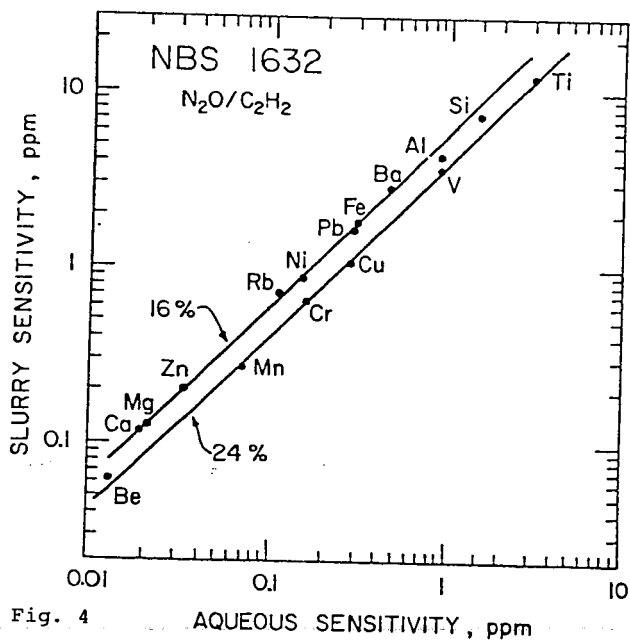
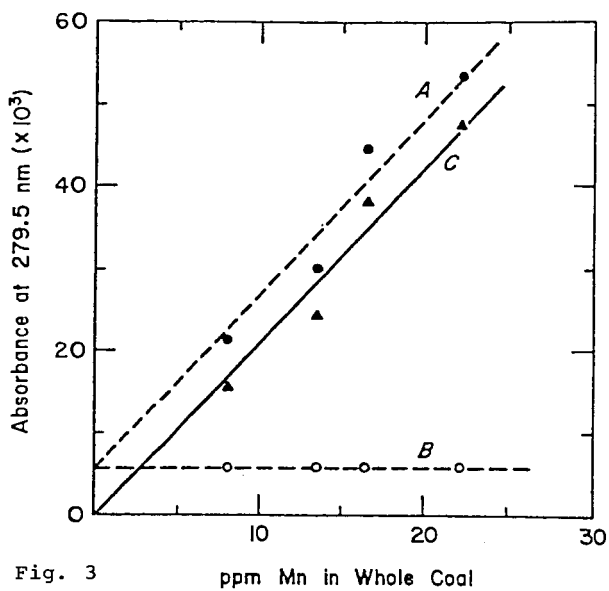
Element	NBS	Slurry-AA	Error, % of NBS
	Concentration, ^b µg/g	Concentration, µg/g	
Si	<u>32000</u>	26000	19
Al	17300*	15700	9
Fe	8700	9200	6
Ca	4340*	4950	14
K	2790*	2570	8
Ti	<u>800</u>	690	13
Na	396*	480	21
Sr	128*	99	22
Cu	18	20	11
Zn	37	34	8
Mn	40	38	5
Ni	15	14	7
Cr	20.2	23	14
Pb	30	24	20
V	35	43	23
Co	5.6*	4.4	21

^aVarious analyzed Kentucky coals were used as standards.

^bUnmarked values are NBS certified, underlined values are NBS provisional;

*values are averages of several reported in the 1977 Illinois State Geological Survey Circular 499 (17).





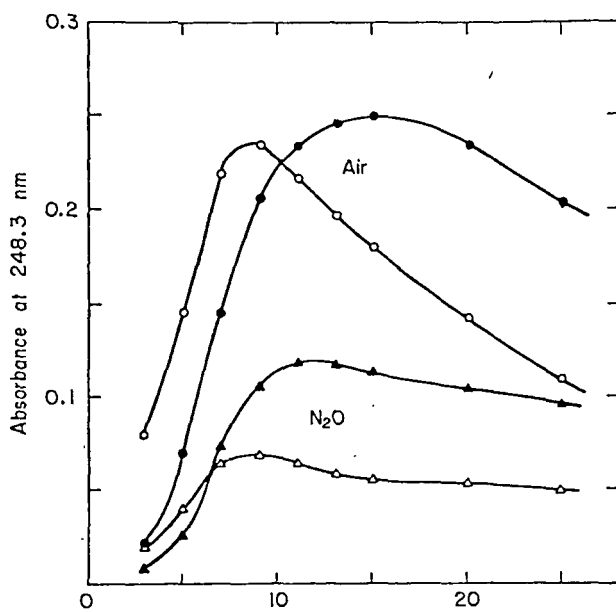


Fig. 5 Height of Measurement, mm above Burner Top

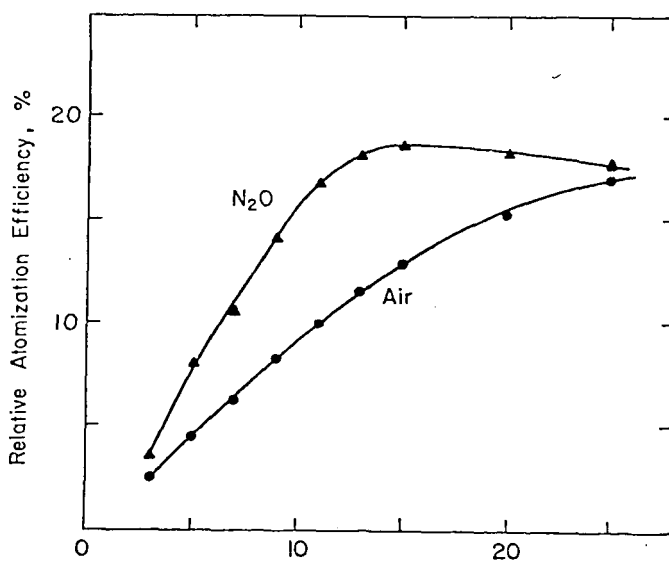


Fig. 6 Height of Measurement, mm above Burner Top